

Viscosity of $[C_4mim][(CF_3SO_2)_2N]$, $[C_4mim][N(CN)_2]$, $[C_2mim][C_2H_5SO_4]$ and $[Aliquat][N(CN)_2]$ in a wide temperature range. Measurement, correlation, and interpretation

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Methyltrialkyl(C_8, C_8, C_{10})ammonium dicyanamide

Aliquat

ABSTRACT

The viscosity of four in-house-made ionic liquids, 1-butyl-3-methyl-imidazolium bis(trifluoromethanesulfonylimide), $[C_4mim][(CF_3SO_2)_2N]$, CAS RN 174899-83-3, 1-butyl-3-methyl-imidazolium dicyanamide, $[C_4mim][N(CN)_2]$, CAS RN 448245-52-1, 1-ethyl-3-methyl-imidazolium ethylsulphate, $[C_2mim][C_2H_5SO_4]$, CAS RN 342573-75-5 and methyltrialkyl(C_8, C_8, C_{10})ammonium dicyanamide $[Aliquat][N(CN)_2]$, CAS RN 63393-96-4, was measured in the temperature range 283.15 K – 373.15 K, at $P = 0.1$ MPa. Data obtained with an absolute relative uncertainty of $U_r(\eta) = 0.02$ was compared with available literature data for all ionic liquids, except for $[Aliquat][N(CN)_2]$, data herein presented for the first time. Both the Vogel-Tammann-Fulcher and IUPAC/IAPWS equations were applied to correlate the measured viscosity data as a function of temperature, the latter being more accurate. Values of η (298.15 K) are recommended for each ionic liquid studied. The viscosities of the different ionic liquids are discussed, considering their chemical structure differences.

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1. Introduction

Ionic liquids are accepted as alternative engineering fluids, capable of replacing, with efficiency and safety, several environmentally harmful solvents, and reagents in the chemical industry [1,2], due to their capacity of being target-designed for a given application. Thermophysical properties are needed for several applications and for the design of chemical plants. Viscosity is extremely important for all flow processes, being however difficult to measure it accurately, for instrumental reasons [3,4] but also, in ionic liquids, because small impurities quantities, namely water, extremely affect its value [5–9]. Moreover, viscosity is also a fundamental property to understanding molecular behaviour, structure,

and usually fairly correlates (in an inverse manner) to ion conductivity and ion self-diffusion coefficients [10].

The dynamic viscosities of four in-house-made ionic liquids (ILs), 1-butyl-3-methyl-imidazolium bis(trifluoromethanesulfonylimide), $[C_4mim][(CF_3SO_2)_2N]$, 1-butyl-3-methyl-imidazolium dicyanamide, $[C_4mim][N(CN)_2]$, 1-ethyl-3-methyl-imidazolium ethylsulphate, $[C_2mim][C_2SO_4]$ and methyltrialkyl(C_8, C_8, C_{10})ammonium dicyanamide $[Aliquat][N(CN)_2]$, were measured in the temperature range 283.15 K – 373.15 K, at $P = 0.1$ MPa.

One of the compounds studied, $[Aliquat][N(CN)_2]$ deserves a comment, already explained in a previous publication [1]. The designation Aliquat refers not to a pure cation, methyltriocetylammmonium dicyanamide, but to a complex mixture of cations, where three of the alkyl chains have different number of carbon atoms - methyltrialkyl(C_8, C_8, C_{10})ammonium. Mass Spectrometry analysis showed that our samples had a five-component mixture of methylhexyldioctylammmonium (0.8%), methyltriocetylammmonium (29.8%), methylodioctyldecylammmonium (43.6%), methyloctyldidecylammmonium (21.9%), and methyltridecylammmonium (3.8%). Although in

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the literature the designation aliquat appears for different cations, we prefer to designate our compound as [Aliquat 336®-derived][N(CN)₂] or [Aliquat][N(CN)₂] as a short name [1].

This work complements values of density, infinite dilution diffusion coefficient, heat capacity, surface tension, thermal expansion coefficient and isothermal compressibility previously published by some of us [1], to include a paramount diversity of fundamental properties to be used for heat and mass transfer in sustainable processes.

2. Material and methods

The ionic liquids studied were synthesized at the organic chemistry laboratories of the Centro de Química-Física Molecular (IST, UTL) following general reported procedures for 1-butyl-3-methyl-imidazolium chloride, [C₄mim][Cl], precursor [3], [C₄mim][(CF₃SO₂)₂N] [5], [C₄mim][N(CN)₂] [10], [C₂mim][C₂SO₄] [11] and [Aliquat][N(CN)₂] [12]. Further details about their synthesis, purification and characterization are described in detail in Table 1 of the previous publication [1]. The water content of the samples after drying in high vacuum (typically 1 Pa) and at moderate temperatures (typically 320 K) were determined by coulometric Karl-Fisher titration (Metrohm 831KF Coulometer), and are, <120 ppm, <110 ppm, <100 ppm, and <120 ppm, respectively.

The measurements of viscosity were performed using an automated SVM 3000 Anton Paar rotational Stabinger viscometer-densimeter, in the temperature range of (278.15–373.15) K at atmospheric pressure. The temperature uncertainty is $u(T) = 0.02$ K, the pressure uncertainty is $u(P) = 1$ kPa, the relative uncertainty of the dynamic viscosity is $u_r(\eta) = 0.01$ and the absolute uncertainty of the density is $u(\rho) = 0.5$ kg·m⁻³. Further details about the equipment, methodology and associated uncertainties can be found elsewhere [13].

3. Results and discussion

The viscosity data obtained for the four ionic liquids are reported in Table 1 and illustrated in Fig. 1 for the four studied ILs. The Vogel-Fulcher-Tammann equation (VFT) [14,15] (Eq. (1)), suitable for glass-forming liquids, was applied to correlate the viscosity experimental data with temperature,

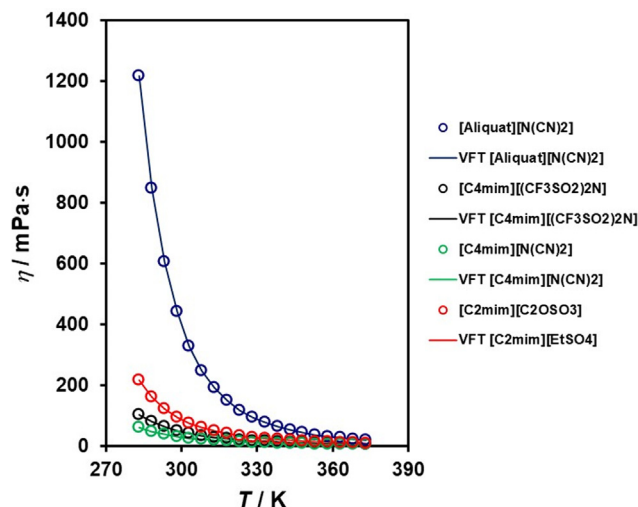


Fig. 1. Viscosity, η of the studied ILs as a function of temperature: (○) [C₄mim][(CF₃SO₂)₂N], (○) [C₄mim][N(CN)₂], (○) [Aliquat][N(CN)₂], (○) [C₂mim][C₂SO₄]. The solid lines represent the correlation of the experimental data using Eq. (1).

$$\eta = Ae^{B/(T-C)} \quad (1)$$

where η is the viscosity in mPa·s, T is the temperature in K and A , B and C are adjustable parameters. The performance of the obtained correlation is illustrated in Fig. 1 and the values of the A , B and C parameters and AAD are displayed in Table 2. The maximum deviation between experimental values and those calculated by Eq. (1) is -0.47% for [Aliquat][N(CN)₂] at the lowest temperature. In general, for the other three ILs studied the largest deviations are found for the highest temperatures. The parameter C was related by Angell and Sage [14] to the glass temperature transition, T_g , present in the ionic liquids, corresponding to a temperature for which viscosity becomes infinite. Since this work, many authors have measured T_g , especially for [C₄mim][(CF₃SO₂)₂N], for which 9 data sets were found, while for [C₄mim][N(CN)₂] and [C₂mim][C₂SO₄] 3 and 5 data sets were found, respectively, and for comparison, an average value was calculated. Table SM1 in Supplementary Material, displays the values encountered, including all references. The values found were

Table 1

Experimental viscosities, η , for [C₄mim][(CF₃SO₂)₂N], [C₄mim][N(CN)₂], [Aliquat][N(CN)₂] and [C₂mim][C₂SO₄], as a function of temperature, at $P = 0.1$ MPa.^a

T/K^b	[C ₄ mim][(CF ₃ SO ₂) ₂ N] $\eta^c/\text{mPa}\cdot\text{s}$	[C ₄ mim][N(CN) ₂] $\eta^c/\text{mPa}\cdot\text{s}$	[Aliquat][N(CN) ₂] $\eta^c/\text{mPa}\cdot\text{s}$	[C ₂ mim][C ₂ SO ₄] $\eta^c/\text{mPa}\cdot\text{s}$
283.15	103.58	60.46	1216.47	217.76
288.15	79.76	47.40	848.79	161.03
293.15	62.67	37.91	605.77	121.95
298.15	50.17	30.90	441.46	94.42
303.15	40.80	25.56	327.95	74.55
308.15	33.67	21.45	248.00	59.89
313.15	28.15	18.23	190.58	48.87
318.15	23.82	15.66	148.70	40.43
323.15	20.36	13.59	117.66	33.88
328.15	17.58	11.90	94.36	28.72
333.15	15.31	10.51	76.55	24.60
338.15	13.44	9.35	62.79	21.26
343.15	11.89	8.37	52.06	18.53
348.15	10.58	7.54	43.56	16.28
353.15	9.47	6.83	36.78	14.41
358.15	8.53	6.22	31.31	12.83
363.15	7.72	5.69	26.87	11.49
368.15	7.02	5.23	23.21	10.35
373.15	6.40	4.83	20.19	9.37

^a $u(P) = 1$ kPa.

^b $u(T) = 0.02$ K.

^c $u_r(\eta) = 0.02$.

Table 2

Correlation parameters A, B and C of Eq. (1) for the viscosity the studied ILs as a function of temperature.

	A	B	C	AAD/%	T _g
[C ₄ mim][[(CF ₃ SO ₂) ₂ N]	0.16502	763.17	164.67	0.06	185.30 ^a
Water-free	0.16789	757.55	165.35	0.08	
[C ₄ mim][N(CN) ₂]	0.20856	635.10	171.10	0.08	180.58 ^b
Water-free	0.20625	638.51	170.75	0.11	
[C ₂ mim][C ₂ SO ₄]	0.19355	780.22	172.10	0.03	185.95 ^c
Water-free	0.19715	775.08	172.60	0.05	
[Aliquat][N(CN) ₂]	0.03813	1425.4	145.76	0.19	183.21 ^d

^a Average of all 9 data sets presented in Table SM1 of Supplementary Material.^b Average of 3 data sets presented in Table SM1 of Supplementary Material.^c Average of 5 data sets presented in Table SM1 of Supplementary Material.^d Reference in Table SM1 of Supplementary Material.

T_g = 185.30 K for [C₄mim][[(CF₃SO₂)₂N], T_g = 180.58 K for [C₄mim][N(CN)₂], T_g = 185.95 K for [C₂mim][C₂SO₄] and T_g = 183.21 K for [Aliquat][N(CN)₂], all very close to each other. Since the C parameter is similar for most of the ILs, some authors take it as constant and equal to 165.06 K [16,17]. However, if this might be useful for generalized equations, Table 2 shows that the values of C vary between 145.76 K and 172.10 K for our ILs, values around 10–20 K below the reported glass temperature. It must be remembered that these experimental values of the glass temperature are determined by Differential Scanning Calorimetry or by Thermal Gravimetric Analysis, and therefore the uncertainty is never smaller than 3 K, depending on the temperature scanning rates used (see, e.g., in Table SM1, the standard deviation of the mean for [C₂mim][C₂SO₄], 8 K).

The comparison of the present data with literature was based in the published data registered in the NIST Database ILThermo (v2.0) [18]. All temperature data refers to ITS-90. This comparison will be done separated for each ionic liquid. In Supplementary data all data sets and their sources are described, including Literature source, Technique, Temperature Range/K, Pressure Range/MPa, No. of Data Points, Assigned Uncertainty [In the presented tables, the assigned uncertainty is the claimed by the authors, corrected, when applicable, to expanded global uncertainty (relative or absolute), at 95% confidence level, (k = 2)], Sample Origin and Water Content.

For [C₄mim][[(CF₃SO₂)₂N] forty eight data sets were found, using capillary tube (Ostwald or Ubbelohde) viscometry, cone and plate viscometry, concentric cylinders viscometry, falling or rolling sphere viscometry and moving piston method, with assigned uncertainties from

U_r(η) = 0.011–0.29, from samples synthesized at authors laboratories or commercial. All the information available is present in Table SM2, including original references. Fig. 2 compares the viscosity results obtained in this work with the available literature data, having Eq. (1) as the reference. Data with deviations greater than ±10% are not shown. This is the case of Huddleston et al. (2001), using a capillary tube with an assigned uncertainty of 29% and deviations of +37.5%, McFarlane et al. (2005) working with a cone and plate rheometer with an assigned uncertainty of 6.0% and deviations between –12% and +16%, Zhang et al. (2007) working with a concentric cylinder viscosimeter, with an assigned uncertainty of 2.3% but deviations of –12.7%, and Gelinas et al. (2016) obtained with a moving piston method, without claimed uncertainty or sample purity information, and deviations of –12.8%. It is clear from this figure that most of the data fall within ± 5% deviations from our equation, exceptions for the data of Chen et al. (2008), obtained with a concentric cylinder viscometer and assigned uncertainty of 30% and deviations up to –9%, Kakimura et al. (2017), obtained with a concentric cylinder viscometer, with an assigned uncertainty of 10.4%, and deviations up to

–10%, Yadav et al. (2018), obtained with a falling ball viscometer and assigned uncertainty of 4.4% and deviations up to –8% and some data points, not systematic, from other authors. Also present are the data reported in this paper.

These data have different water contents in the samples measured. Therefore, in order to have a better view of the correct agreement between the published data, we obtained “water-free” viscosity values, following a methodology described by Widegren and Magee (2007) [7], Santos et al. (2010) [19], Queirós et al. (2020) [20] and Paredes et al. (2020) [9], following eq (2), valid for small contents in water:

$$\eta_{wf} = \eta_{wf}(0, T) = \eta_{exp}(x, T) - \left(\frac{\partial \eta}{\partial x} \right)_T x \quad (2)$$

Here η_{wf} is the “water free” value of the viscosity of the ionic liquid, for the molar fraction of water in the ionic liquid, x. The value of the derivative $\left(\frac{\partial \eta}{\partial x} \right)_T$ was estimated at each temperature from the published data on the viscosity of [C₄mim][[(CF₃SO₂)₂N] + water mixtures, reported by Widegren et al. (2005) [18], Lopes et al. (2011) [21], Andanson et al. (2016) [22] and Alcalde et al. (2018) [23], and extrapolated for $x = 0$, $\lim_{x \rightarrow 0} \left(\frac{\partial \eta}{\partial x} \right)_T$. These values are function of temperature, and were fitted for 283.15–323.15 K to a function of the type:

$$\lim_{x \rightarrow 0} \left(\frac{\partial \eta}{\partial x} \right)_T = \sum_{i=0}^{i=j} c_i T^{-i} \quad (3)$$

for j = 2 and used to correct all the experimental data with reference to water content of the samples, including present data. This function is near zero for temperatures above 330 K and can be extrapolated without significant error up to 393 K, the highest temperature measured so far, by Tariq et al. (2011) [13], is represented in Fig. 3a. As this ionic liquid is not a strong absorbent of water, the corrections are small, around 0.6% for our data, with samples with w_{H2O} = 0.00012 (x_{H2O} = 0.00279).

Fig. 4 shows the deviations of the literature “water-free” data from our Vogel-Fulcher-Tammann equation (VFT) fit for the “water-free” values, reported in Table 3. Coefficients of this equation are also shown in Table 2. Only results with deviations smaller than 5% are shown. The agreement between the data reported in Fig. 4 is very satisfactory, being excellent and within mutual uncertainty (~2%) with many sets of data. We can conclude that our data represents an excellent representation as a function of temperature of the viscosity of [C₄mim][[(CF₃SO₂)₂N], in the temperature range (278.15–373.15) K, with an uncertainty U_r = 0.02.

For [C₄mim][N(CN)₂] sixteen data sets are available in the literature, using capillary tube (Ostwald or Ubbelohde) viscometry, concentric cylinders viscometry and moving piston method, with assigned uncertainties from U_r(η) = 0.011 to 0.11, from samples synthesized at authors laboratories or commercial. All the informa-

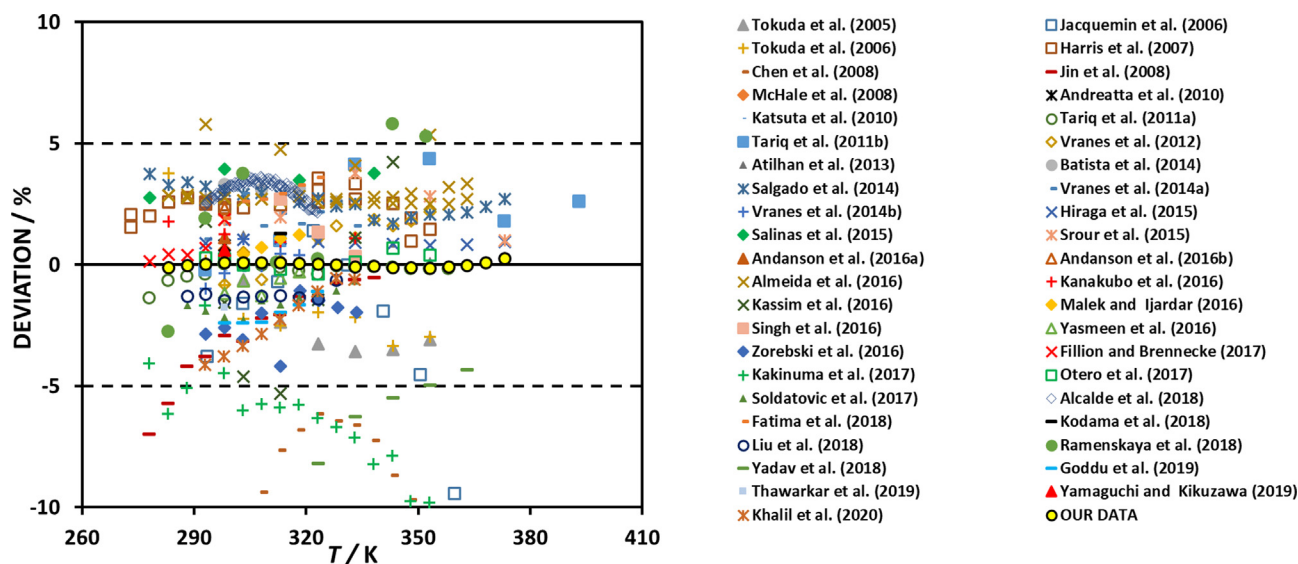


Fig. 2. Deviations from the available $[\text{C}_4\text{mim}][(\text{CF}_3\text{SO}_2)_2\text{N}]$ viscosity data from Eq. (1). Present data are also shown.

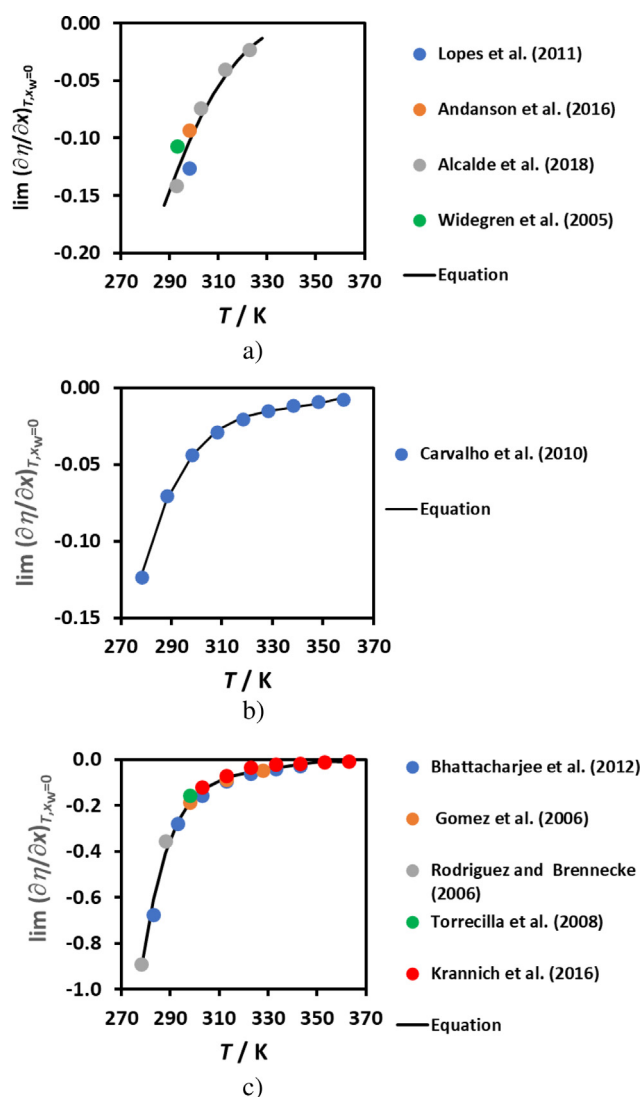


Fig. 3. The function $\lim (\partial \eta / \partial x)_{T, x_w=0}$ as a function of temperature, in Pa.s, for a) $[\text{C}_4\text{mim}][(\text{CF}_3\text{SO}_2)_2\text{N}]$; b) $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$; c) $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$.

tion available and the data references are present in Table SM3. Fig. 5 compares the viscosity results obtained in this work with the available literature data, having Eq. (1) as the reference. Data with deviations greater than $\pm 15\%$ are not shown. This is the case of Fendt et al. (2011), using a concentric cylinders viscometer, with an assigned uncertainty of 6.5% and deviations up to + 61%, and some data points of Sanchez et al. (2009), obtained with a capillary tube, with an assigned uncertainty of 2.7% and deviations up to -32.8% . It is clear from this figure that data of Kakinuma et al. (2017), obtained with a moving piston method, with an assigned uncertainty of 5.4% has a systematic deviation between -10 and -12% for temperatures up to 340 K, then decreasing to -4% at 353 K, and the remaining points of Sanchez et al. (2009) have a totally different temperature coefficient. Fig. 4 also displays the data presented in this paper, at the base line.

As the data have also different water contents from our samples, $w_{\text{H}_2\text{O}} = 0.00011$ ($x_{\text{H}_2\text{O}} = 0.00253$), the same methodology described above was applied to obtain viscosity “water-free” values. Two sets of viscosity of $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ + water mixtures were found, by Carvalho et al. (2010) [16] and Havlov and Dohnal (2018) [24]. However, these last data cover compositions very distant from infinite dilution, so where not used in the extrapolation to zero water content. Data of Carvalho et al. (2013) [16] was extrapolated for $x = 0$, $\lim_{x \rightarrow 0} (\partial \eta / \partial x)_T$ and then fitted to a function given by Eq. (3), for $j = 3$. The variation of this function with temperature is shown in Fig. 3b. Eq. (2) was then used to correct all the experimental data with reference to water content of the samples, including present data. Deviations from our Vogel-Fulcher-Tammann equation (VFT) fit for the “water-free” values, reported in Table 2, are shown in Fig. 6. Coefficients of this equation are also shown in Table 2. Only results with deviations smaller than 5% are shown. The magnitude of the corrections is very small, around 0.2% for our data at the lowest temperature.

Several sets deviate from our data by more than the mutual uncertainty, namely at temperatures below 300 K, either positive like data of Carvalho et al. (2010) [16] or negative, like data of Engelmann et al. (2012) [25], Calado et al. (2015) [26] and Almeida et al. (2016) [27]. Above 300 K all the data agrees with our data within their mutual uncertainties. No reason was detected for these discrepancies, as the purity and water content of the samples used are similar to ours. However, this might be possibly attributed to problems in temperature control in the measuring cells at the

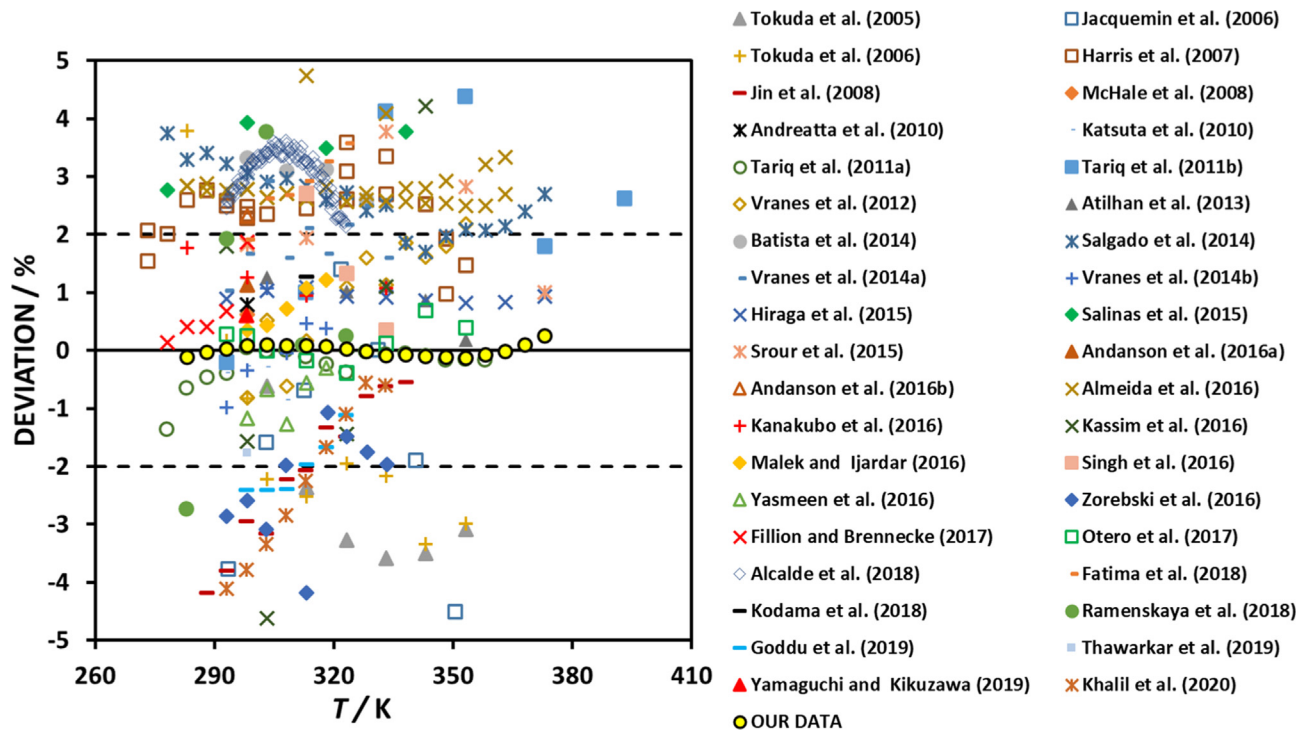


Fig. 4. Deviations from the available [C4mim][(CF3SO2)2N] “water-free” viscosity data from Eq. (1). Present data are also shown. The dashed lines represent the value of our data uncertainty, $U_r = 0.02$.

Table 3
Water-free viscosities, η_{wfr} , for [C4mim][(CF3SO2)2N], [C4mim][N(CN)2], [Aliquat][N(CN)2] and [C2mim][C2SO4], as a function of temperature, at $P = 0.1$ MPa.^a Values at 298.15 where used in Eq. (4).

T/K^b	[C4mim][(CF3SO2)2N] $\eta^c/\text{mPa}\cdot\text{s}$	[C4mim][N(CN)2] $\eta^c/\text{mPa}\cdot\text{s}$	[C2mim][C2SO4] $\eta^c/\text{mPa}\cdot\text{s}$
283.15	104.12	60.57	218.56
288.15	80.20	47.49	161.56
293.15	63.03	37.98	122.31
298.15^d	50.45	30.95	94.67
303.15	41.02	25.60	74.72
308.15	33.84	21.49	60.01
313.15	28.28	18.25	48.97
318.15	23.91	15.69	40.51
323.15	20.42	13.62	33.95
328.15	17.62	11.92	28.78
333.15	15.32	10.53	24.65
338.15	13.45	9.37	21.30
343.15	11.89	8.39	18.56
348.15	10.58	7.56	16.30
353.15	9.47	6.84	14.42
358.15	8.53	6.23	12.84
363.15	7.73	5.70	11.51
368.15	7.04	5.23	10.38
373.15	6.45	4.83	9.43

^a $u(P) = 1$ kPa.
^b $u(T) = 0.02$ K.
^c $U_r(\eta) = 0.02$.
^d Recommended values at 298.15 in bold.

lower temperatures. The “water-free” values for the viscosity of [C4mim][N(CN)2] are presented in Table 3. We can conclude that our data represents an excellent representation as a function of temperature of the viscosity of [C4mim][N(CN)2], in the temperature range (278.15 to 373.15) K, with an uncertainty $U_r = 0.02$.

For [C2mim][C2SO4] twenty six data sets are available in the literature, using capillary tube (Ostwald or Ubbelohde) viscometry, concentric cylinders viscometry, rolling sphere viscometry, vibrat-

ing wire viscometry, surface light scattering and moving piston method, with assigned uncertainties from $U_r(\eta) = 0.018$ to 0.17, from samples synthesized at authors laboratories or commercial. All the information available and the data references are present in Table S3. Fig. 7 compares the viscosity results obtained in this work with the available literature data, having Eq. (1) as the reference. Data with deviations outside the interval +10% to −6% are not shown. This is the case of Majhi et al. (2016) [28], using a cone and plate viscometer, with an assigned uncertainty of 2.0%, and deviations up to −31%, probably to deficient operation of the rheometer. This figure shows that several data sets have positive deviations in relation to our data, as high as +8% at the lower temperatures. This might be an artifact for temperatures below 283 K, the lower limit of the VFT correlation, extrapolated down to 255 K. However, some data have negative deviations, and other with excellent agreement with our data, to within $\pm 2\%$, cases of Pereiro et al. (2012) [29], Fernandez et al. (2008) [30], Pinto et al. (2014) [31] and Anwar and Riyazuddeen (2017) [32], and some data, for temperatures 310 K of other authors.

All data reported has water contents which differ from our samples, $w_{H2O} = 0.00010$ ($x_{H2O} = 0.00131$). The same methodology described above was applied to obtain viscosity “water-free” values. Five sets of data on the viscosity of [C2mim][C2SO4] + water mixtures were obtained from literature, namely those of Gomez et al. (2006) [33], Rodriguez and Brennecke (2006) [34], Torrecilla et al. (2008) [35], Bhattacharjee et al. (2012) [36] and Krannich et al. (2016) [37], which cover compositions for low water content. These data was extrapolated for $x = 0$, $\lim_{x \rightarrow 0} (\frac{\partial \eta}{\partial x})_T$ and fitted to a function given by Eq. (3), for $j = 4$, for $278.15 < T(K) < 363.15$. The variation of the obtained function is shown in Fig. 3c, and it is clear that its value is bigger than for the previous ionic liquids, a factor of five or more, especially at the lower temperatures. The “water-free” values for the viscosity of [C2mim][C2SO4] are also presented in Table 3.

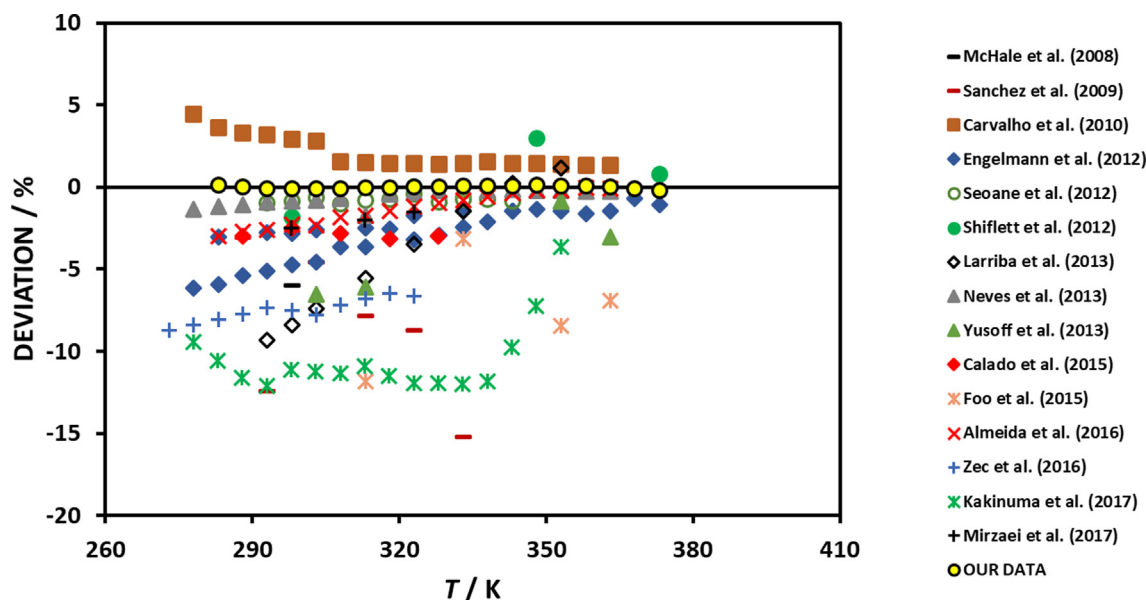


Fig. 5. Deviations from the available $[C_4mim][N(CN)_2]$ viscosity data from Eq. (1). Present data are also shown.

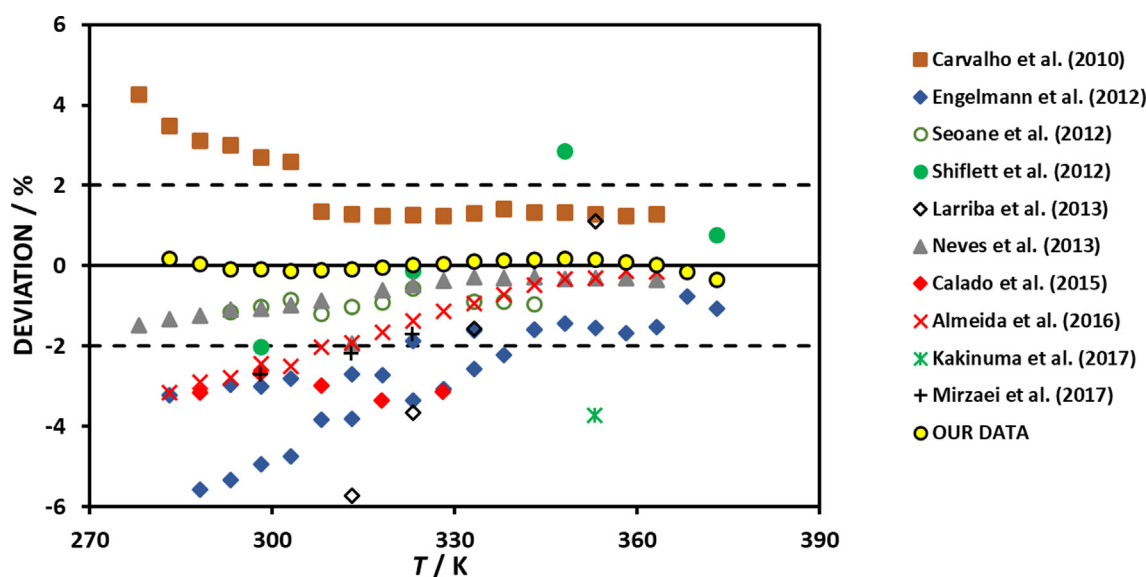


Fig. 6. Deviations from the available $[C_4mim][N(CN)_2]$ "water-free" viscosity data from Eq. (1). Present data is also shown. The dashed lines represent the value of our data uncertainty, $U_r = 0.02$.

Deviations from our Vogel-Fulcher-Tammann equation (VFT) fit for the "water-free" values, reported in Table 2, are shown in Fig. 8. Coefficients of this equation are also shown in this table. Only results with deviations -6% and $+10\%$ are shown. The magnitude of the corrections is more significant, around 0.4% for our data at the lowest temperature. It is clear from this figure that the comparison is different, for the data that agrees with ours to within 2% , twice our expanded relative uncertainty. This is the case for most of the points of Fernandez et al. (2008) [30], Rodriguez and Brennecke (2006) [34], high temperature points of Schmidt et al. (2012) [38], Pinto et al. (2014) [31] up to 338 K , Anwar and Riyazuddeen (2017) [32] and Zivkovic et al. (2018) [39]. Our data represents an excellent representation as a function of temperature of the viscosity of $[C_2mim][C_2SO_4]$, in the temperature range (278.15 to 373.15 K), with an uncertainty $U_r = 0.02$.

For the viscosity of $[Aliquat][N(CN)_2]$, only our data is available in the literature. Fig. 9 shows the deviations of our data to the VFT fit, Eq. (1), which coefficients are also displayed in Table 2. As already explained in a recent publication by some of the authors [9], Vogel-Tammann-Fulcher is not the best form to analyze the dependence of viscosity on temperature of ionic liquids, although it is claimed by some authors, as for example Angell and Share (1970) [14] and Navia et al. (2005) [15] among others, that interpret the parameter C as a glass transition temperature, it has been very difficult to correlate the value found for each ionic liquid with its molecular structure. All the ionic liquids studied here present a deviation plot sigmoid shaped as that shown in Fig. 9 for $[Aliquat][N(CN)_2]$.

An equation recommended for the variation of standard reference data by IUPAC [40,41] and for the viscosity of water by IAPWS [42,43] represents much better the curvature of the experimental

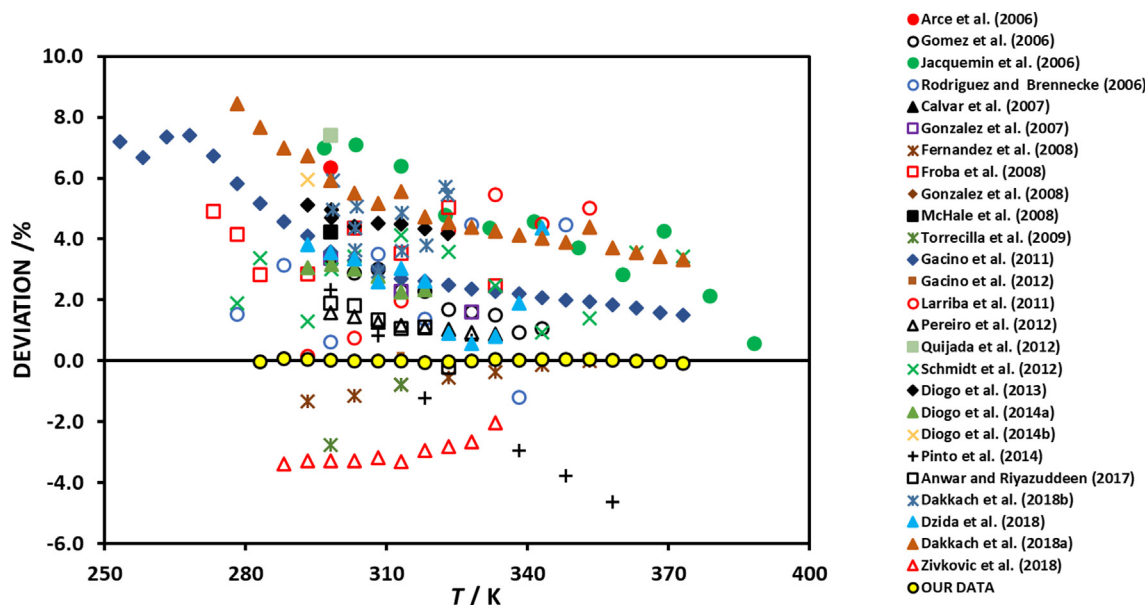


Fig. 7. Deviations from the available $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$ viscosity data from Eq. (1). Present data are also shown.

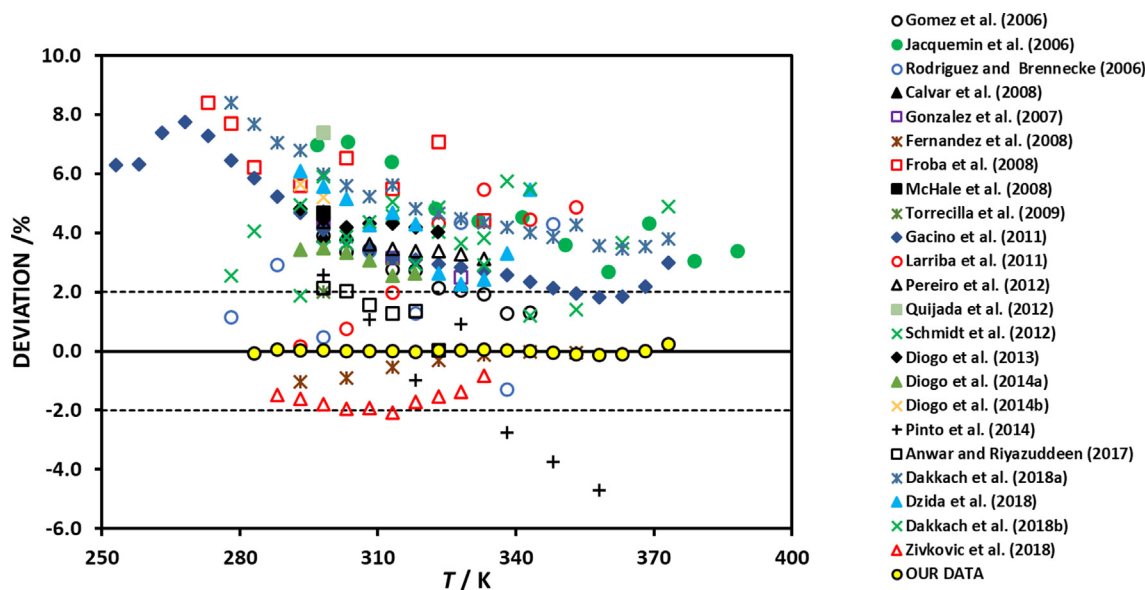


Fig. 8. Deviations from the available $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$ "water-free" viscosity data from Eq. (1). Present data is also shown. The dashed lines represent the value of our data uncertainty, $U_t = 0.02$.

data dependence of temperature and was applied recently to the viscosity, electrical conductivity and ion self-diffusion coefficient of $[\text{C}_6\text{mim}][(\text{CF}_3\text{SO}_2)_2\text{N}]$, the IUPAC reference ionic liquid [8], to define reference data and reference equations for these properties [9], and to the viscosity of $[\text{C}_4\text{mim}][(\text{C}_2\text{F}_5)_3\text{PF}_3]$, in comparison with several other equations, including VFT [44]. This equation was adopted by IUPAC and IAPSW, and has the form:

$$\ln \eta^* = \sum_{i=0}^{i=j} A_i (T^*)^{-i} \quad (4)$$

where η^* and T^* are the dimensionless variables defined as:

$$\begin{aligned} T^* &= T(\text{K})/298.15\text{K} \\ \eta^* &= \eta(T)/\eta(298.15\text{K}) \end{aligned} \quad (5)$$

The number of coefficients A_i was optimized for each ionic liquid, with $j = 4$ for all. Their values, standard deviations and AAD/% of each fit is given in Table 4. Values of η (298.15 K) were taken from our water-free experimental data, for each fluid, and are highlighted in Table 3. It is clear that the values of AAD are much smaller than in the VFT equation (Table 2) for all the four ionic liquids. Fig. 10 shows the deviations of the water-free experimental data from Eq. (4), as a function of temperature. Deviations are random (not systematic and no trend) and do not amount by more than 0.06%, except for some points for $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$, that can reach 0.1%.

As expected, the three imidazolium-based ILs measured in this work display much lower viscosity values than the $[\text{Aliquat}][\text{N}(\text{CN})_2]$, which is clearly linked to the large alkyl chains (C8 and

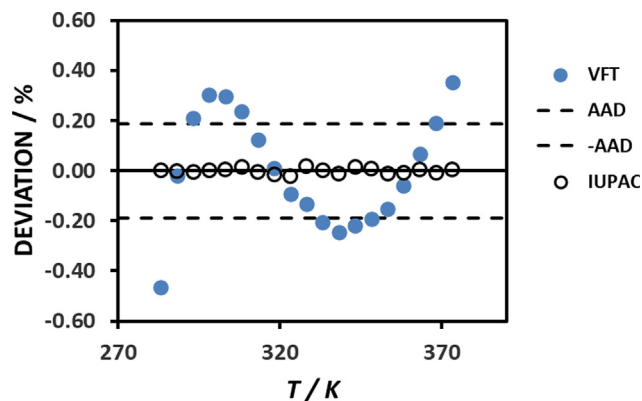


Fig. 9. Deviations of the experimental points for [Aliquat][N(CN)₂] from the VFT fit. Dashed lines represent the boundaries of the AAD value. Also shown deviations using IUPAC Eq. (4).

C10) of this IL, a five-component mixture of methylhexyldioctylammonium (0.8%), methyltrioctylammonium (29.8%), methyl-dioctyldecylammonium (43.6%), methyl-octyldidecylammonium (21.9%), and methyltridecylammonium (3.8%) [1]. The increase in the viscosity with the increase of the alkyl side-chains length of the cation in the imidazolium-based ionic liquids is well documented. Two main explanations have been forward for this fact: the increase of van der Waals interactions between alkyl side-chains of the cations in the homologous series [45] and the formation of nano-structural domains permeated by charged/polar network for ionic liquids with alkyl chain length longer than C₆ [46]. On the other hand, the increase of the length of the alkyl sidechains leads to a larger hydrodynamic radius and thus a smaller mobility, less fluidity and higher viscosity.

Within the imidazolium family the viscosity increases in the following order of the anions [N(CN)₂] < [(CF₃SO₂)₂N] < [C₂SO₄], for the same cation. Ionic liquids with dicyanamide ion, [N(CN)₂][−], are known to be among the ILs with the smallest viscosities, as with [SCN][−] and [C(CN)₃][−] ions [44,47], having interesting properties for industrial applications, namely as heat transfer fluids [48]. Viscosities of almost all members of the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide family were reported in the temperature range between 278.15 and 393.15 K, by Tariq et al. [13] concluded that for short chain ILs the formation of nano-domains is not possible as the non-polar part is not large enough. The formation of such nano-segregated domains can also contribute to the increase in viscosity. The bis(trifluoromethanesulfonylimide) anion, [(CF₃SO₂)₂N], a bulkier anion than the cyano-ions, creates less mobility to the ionic liquid and therefore contributes to a higher viscosity. For ethylsulfate anion, [C₂SO₄], viscosity increases due to sulfur atom (greater anion size) and to the possibility of forming clusters/aggregates between the anions, which restricts the mobility and the self-diffusion coefficient of the ion, therefore increasing the viscosity. So does the possibility of stronger molecular interactions due to hydrogen bonding [49].

Table 4

Correlation parameters A_i of Eq. (4) for the water-free viscosity of the studied ILs as a function of temperature.

Ionic Liquid	A ₀	A ₁	A ₂	A ₃	A ₄	AAD/%
[C ₄ mim][[(CF ₃ SO ₂) ₂ N]	11.70207 ± 0.94929	−74.38819 ± 4.13722	130.2226 ± 6.7435	−96.87852 ± 4.87219	29.34182 ± 1.31655	0.0088
[C ₄ mim][N(CN) ₂]	−9.00119 ± 1.31981	12.84325 ± 5.75202	−3.49612 ± 9.37561	−7.28808 ± 6.77386	6.94195 ± 1.83041	0.0137
[C ₂ mim][C ₂ SO ₄]	13.54652 ± 4.30112	−87.28607 ± 18.74531	156.8101 ± 0.5542	−120.6000 ± 2.07535	37.52933 ± 5.96515	0.0471
[Aliquat][N(CN) ₂] ^a	−14.93634 ± 0.84078	32.04042 ± 3.66432	−45.51776 ± 5.97272	36.37641 ± 4.31527	−7.96274 ± 1.16606	0.0006

^a Raw data.

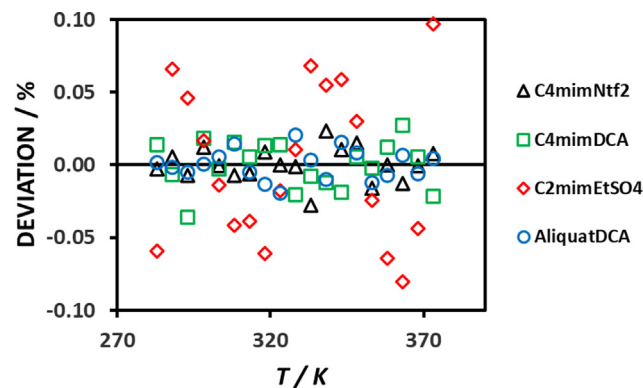


Fig. 10. Deviations of the water-free experimental points from IUPAC equation, Eq. (4), for all ionic liquids studied, as a function of temperature.

4. Conclusions

The viscosity of four in-house-made ionic liquids (ILs), [C₄mim][[(CF₃SO₂)₂N], [C₄mim][N(CN)₂], [C₂mim][C₂H₅SO₄] and [Aliquat][N(CN)₂], was measured in the temperature range 283.15 K–373.15 K, at P = 0.1 MPa, ranging from 4.83 to 1216 mPa·s. Data for the viscosity of [Aliquat][N(CN)₂], a five-component mixture of methylhexyldioctylammonium (0.8%), methyltrioctylammonium (29.8%), methyl-dioctyldecylammonium (43.6%), methyl-octyldidecylammonium (21.9%), and methyltridecylammonium (3.8%) is presented for the first time. The three imidazolium based ILs measured in this work display much lower viscosity values than the [Aliquat][N(CN)₂], which is clearly linked to the large alkyl chains (C8 and C10) in the nitrogen atom of this IL.

Data was compared with literature, using water-free values, by correcting the estimated water content of all the samples studied, by us and available in the literature. The Vogel-Tammann-Fulcher was found not to be the best form to correlate the dependence of viscosity on temperature of ionic liquids, the experimental data having been fitted to an equation developed by IUPAC and IAPWS, with AAD smaller than 0.04%.

The viscosity increases with the increase of the alkyl side-chains length of the cation in the imidazolium-based ionic liquids, possibly due to the increase of van der Waals interactions between alkyl side-chains of the cations in the homologous series and to the formation of nano-structural domains permeated by charged/polar network for ionic liquids with alkyl chain length longer than C₆. Increase of the alkyl sidechains leads to a larger hydrodynamic radius and thus a smaller mobility, less fluidity and higher viscosity. Within the imidazolium family the viscosity increases in the following order of the anions [N(CN)₂] < [(CF₃SO₂)₂N] < [C₂SO₄], for the same cation. For the ethylsulfate anion, [C₂SO₄], viscosity increases due to sulfur atom (greater anion size) and to the possibility of forming clusters/aggregates between the anions, which restricts the mobility and the self-diffusion coefficient of the ion,

therefore increasing the viscosity. Hydrogen bonding and stronger interactions also supports this belief.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Authors contribution

LPNR and CANC were responsible for the conception of the project, first draft and final document. MT and JMMSE performed the experimental measurements and processed raw data, also participating in the draft discussions. XP and FJVS, participated with CANC in data analysis, applying the methodology for water-free data, and literature search for comparisons and discussion.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2021.116482>.

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